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THESIS

IDENTIFICATION OF VOLATILE REACTOR FUEL DECOMPOSITION

PRODUCTS BY GAS CHROMATOGRAPHY AND SPECTRAL ANALYSIS

by

Leslie Winfred Cole

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IDENTIFICATION OF VOLATILE REACTOR FUEL DECOMPOSITION

PRODUCTS BY GAS CHROMATOGRAPHY AND SPECTRAL ANALYSIS

by

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Chairman, Department of Material Science
and Chemistry

_____
Academic Dean

ABSTRACT

The gases produced by irradiation of the polyethylene moderated fuel used in the AGN-201 reactor at the Naval Postgraduate School were analyzed for both radioactive and non-radioactive species. The hydrogen content of the gases is higher than that reported in the literature for the radio-induced degradation of polyethylene. Radioactive species identified are Kr^{85m}, Kr^{87}, Kr^{88}, Xe^{133m}, Xe^{133}, Xe^{135}, Xe^{138}, I^{131}, and Cs^{138}. Trace quantities of krypton and xenon were successfully separated without isotopic dilution using gas-solid chromatography.

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ACKNOWLEDGEMENTS

1. Introduction

The polyethylene moderated core of the AGN-201 Nuclear Reactor at the Naval Postgraduate School emits relatively large amounts of gases during and shortly after operation. These gases are subsequently released into the atmosphere. Measuring the constituents of these gases has presented numerous problems to past investigators. The various constituents are gaseous hydrocarbons, fission products, and possibly hydrocarbon-fission product compounds. The reactor fuel, 20% enriched UO_2, is distributed throughout the polyethylene. Operation of the reactor decomposes the polyethylene by radiation and recoil of fission products.

The reactor core and rod voids are pressurized with nitrogen to approximately 1 psig when the reactor is operated. The gas is released periodically so that the total pressure in the core does not exceed 5 psig. The pressure rise is caused by the gaseous products from the degradation of the polyethylene. The radioactivity present in the gas is due to the gaseous fission products which have escaped from the core, but the small amount of these fission products do not add to the pressure.

Several investigators have reported that the bulk of the gas from the radioinduced degradation of polyethylene is hydrogen (1). Laskaris (2), using the same equipment available to this investigator, found that the hydrogen content of the gases was only approximately 50% of the total, with the remainder being light hydrocarbons to C_4. Laskaris also attempted to determine the radioactive constituents by simultaneous gas chromatographic and radioactivity measurements of the gases. He successfully identified some of these constituents.

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Laskaris and others at the Naval Postgraduate School (3,4,5) used gases taken directly from the core of the reactor. The reactor configuration requires the gases to diffuse from the relatively large, solid core through approximately 12 feet of cooper tubing to a sampling manifold. The time necessary for this diffusion effectively prevents measurement of any of the parameters of the gases for several minutes. Additionally, the long copper tube offers a good surface for absorption and perhaps reaction of active species. The gases continue to diffuse from the large core for several hours after a reactor operation. Thus, at any time, there are gases present in the core produced by a prior reaction operation. The effect of the later irradiations on the gases is unknown. It was felt that the hydrocarbon content of the gases was likely to be sensitive to later irradiations.

Further analysis of the gases seemed in order, both to check the drastic deviation in regard to the proportion of hydrogen in the gases emitted from the reactor fuel and to more completely identify the radioactive constituents.

2. Experimental[*]

   a. Production of gases

   In order to evaluate the gases resulting from a particular reactor operation, a small reaction vessel was constructed. This

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[*] Most of the work was done concurrently with Capt. L. A. Lindsay, US Army, whose thesis concerned the analysis of the same gases through a series of half-life studies on individual photopeaks of the radioactive species.

vessel could be placed in the access port in the reactor.[*]
Fuel identical to that in the core of the reactor was placed
in the reaction vessel. The vessel was evacuated to 10^{-4}mm,
and irradiated to obtain sufficient gases for analysis. The
reactor fuel was evacuated prior to each irradiation to insure
that only gases emitted during a single reactor operation
were included in the study. The amount of gases and the
total radioactivity resulting varied with the irradiation
time and power, but no deviation of actual products was found,
for the irradiation variations used.

   b. Measurement of the non-radioactive species

      The same gas chromatograph used by Laskaris was used
in this study. It was necessary to establish the lower limits
of sensitivity of the instrument since the experimental tech-
nique produced only very small samples. Ideally, the sample
size for the instrument should be approximately 0.2 ml at
atmospheric pressure. The pressure of the samples obtained
in the experiment were in the range of 100 to 300 microns.
The low pressure necessitated a sample volume of 2 ml. This
was still much smaller than the ideal sample volume in number
of molecules. This large sample volume with the resulting
back diffusion during sample injection caused considerable
baseline drift and poorly defined peaks.

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   [*]A complete listing of the equipment used in presented is
Appendix I.

c. Measurement of the radioactive species

Several attempts were made to trap the radioactive species separated by the gas chromatograph, both with and without isotopic dilution, but all were unsuccessful.[*] Also, several attempts to measure the radioactive and chromatographic response simultaneously, as had been done by Laskaris, was unsuccessful. Apparently the small sample size with the resulting small amount of activity thwarted all efforts.

Kock and Grandy (6) described a method for separating xenon and krypton. Their method was modified and used in an attempt to separate these two gases from the other radioactive species. A pyrex glass column, approximately 20 by 60 mm was constructed and filled with 40/60 activated charcoal. The column interior and charcoal were evacuated to 10^{-4} mm. The column was connected to the reaction vessel as soon as possible after irradiation (approximately 15 minutes) and cooled to -196° C with liquid nitrogen. Valves on the reaction vessel were opened so the charcoal could absorb the gases for a period of 10 minutes. The reaction vessel was disconnected and helium forced through the charcoal at 400 ml/min. The column was removed from the liquid nitrogen and allowed to come to room temperature as the helium flow started. The effulent gases flowed through a 1/4 in tube and around a 2 by 2 inch scintillation crystal shielded by 2 inches of lead. The crystal acted as a chromatographic detector and its output was monitored by a count rate meter. The effluent

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[*] A method for trapping the gases was later developed but was not attempted with the gases separated with the gas chromatograph.

gases, after passing the scintillation crystal, were forced
into a 3/16 by 6 inch activated charcoal trap cooled to
-196°C. As soon as the first radioactive species had passed,
as indicated on a chromatogram, the charcoal trap was changed.
The charcoal containing the original sample was then heated
rapidly to approximately 300°C. Another peak appeared almost
immediately. The two peaks were subsequently identified as
krypton and xenon, respectively. Gamma ray spectrometry
measurements were made on the radioactive species remaining
in the large column.

3. Results

   a. Non-radioactive species

   Figure 1 is a typical chromatogram measured by Laskaris.
Figure 2 shows a comparative chromatogram measured with the
much smaller sample described above. The general agreement is
excellent. The calculated proportions by volume per cent of
the various hydrocarbons and hydrogen measured by chromatographic
methods are shown in Table I. The values found in this study
compare favorably with those found by Laskaris. The difficulty
in making accurate quantative measurements on a chromatogram
such as Figure 2 tend to make these results less reliable, how-
ever there is a significant amount of hydrocarbons in the gaseous
mixture. This is of importance in view of the reports in the
literature of the much higher content of hydrogen in the degradation
products of polyethylene.

TABLE I

VOLUME PER CENT COMPOSITION OF VOLATILE PRODUCTS

	Laskaris[*]	Cole[*]
Hydrogen	52.5	60.0
Ethane Ethylene	13.0	17
Methane	15.0	19.0
Propane	2.0	1.5
Cyclopropane	1.0	0.5
Propylene	3.5	trace
N-Butane	2.5	1.0
Isobutane	0.5	0.7
2-Butene	0.5	–
1,3-Butadiene	0.5	trace
Acetylene	3.0	trace
Krypton	0.5	–
Xenon	0.5	–

[*]Average of several different runs; does not total 100%
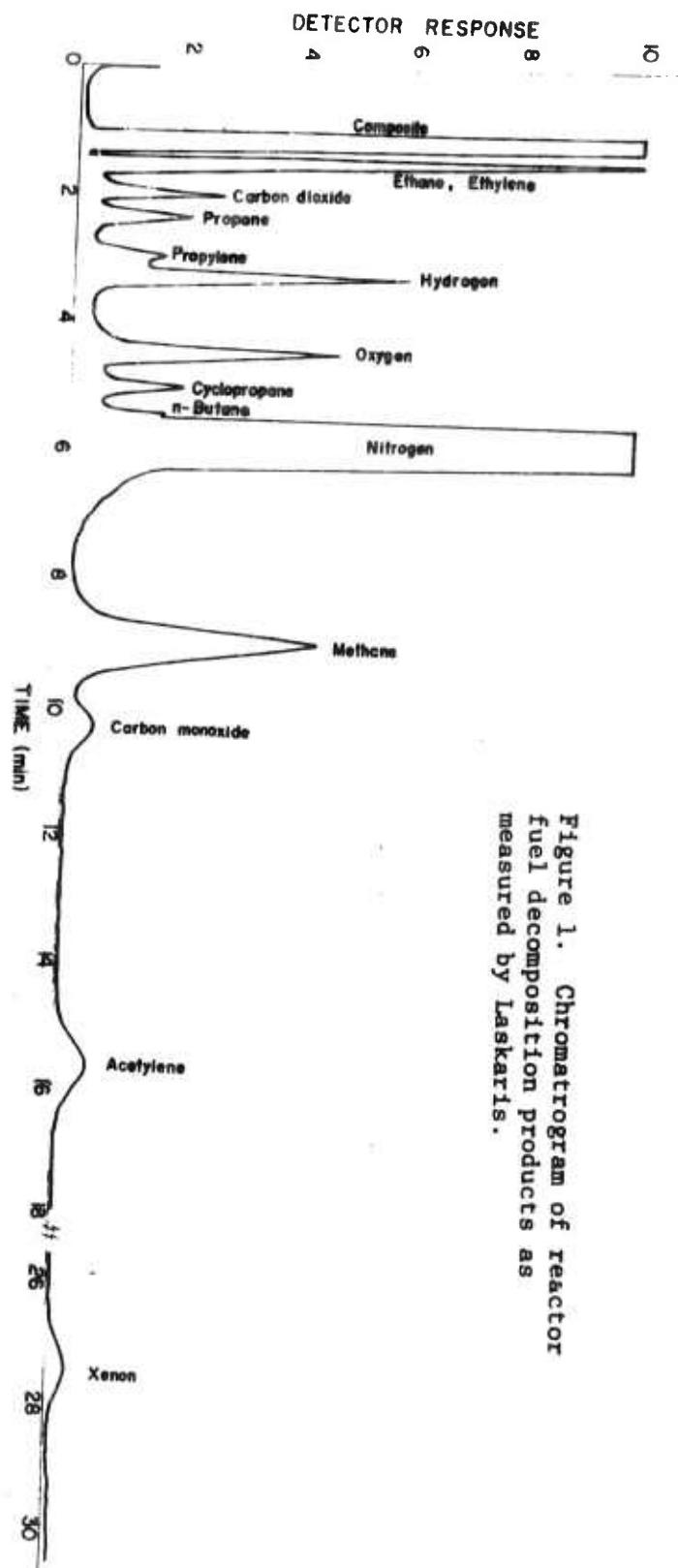
Figure 1. Chromatogram of reactor fuel decomposition products as measured by Laskaris.

Figure 2. Chromatrogram of hydro-
carbons in reactor fuel decomposition
products.
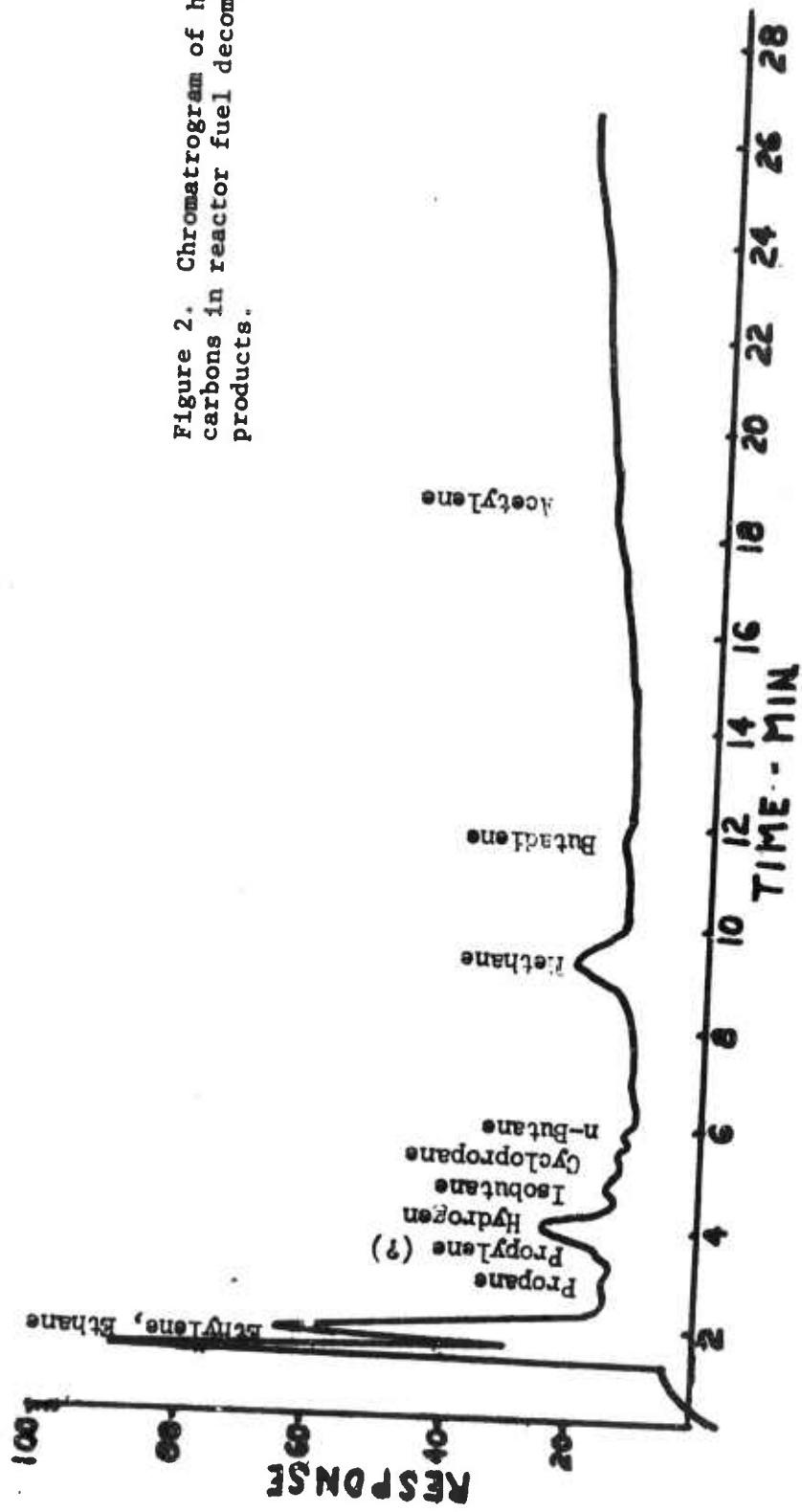
b. Radioactive species

A chromatogram made with the scintillation crystal
detector is shown in Figure 3. The first peak is quite broad
but there is little doubt that it is krypton as shown by the
gamma ray spectrum of the trapped gas (Figure 4). This
spectrum was measured only 2 minutes after the trap was removed
from the chromatograph and only 36 minutes after the irradiation
had been completed. The second peak is much sharper as the
result of the much higher temperature while it was being eluted.
A gamma ray spectrum of this gas is shown in Figure 5. This
measurement was made 51 minutes after the irradiation and 15
minutes after separation. Xenon and some of its decay products
are clearly identifiable.

Gamma ray spectra of the separated gases taken at later
times revealed no radioactive species other than the krypton
or xenon and their decay products. Also no other radioactive
species could be eluted from the original sample in 30 minutes
at $300^{\circ}C$.

The first peak could possibly be made sharper and could
have been eluted earlier at a somewhat higher temperature.
This was not attempted as the separation seemed adequate. Dal
Nogare and Juvet discuss the effect of increased temperature
on elution time and peak sharpness (6). A point of particular
note about this separation is that the gases present were only
those present as the result of the irradiation of the fuel.
Isotopic dilution was not necessary for the separation.

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Figure 3. Chromatrogram of radio-
active gases in reactor fuel
decomposition products.

TIME - MIN

RESPONSE

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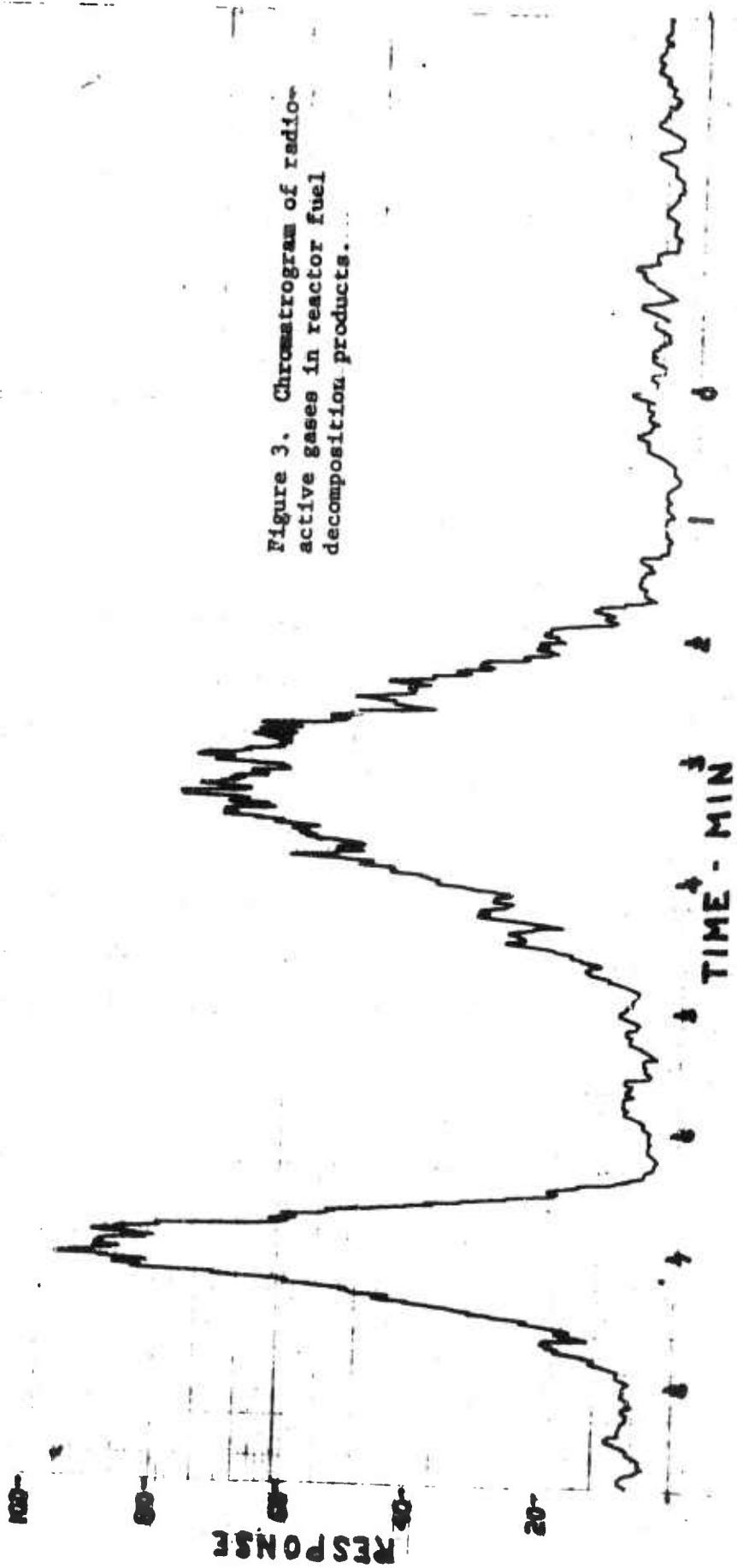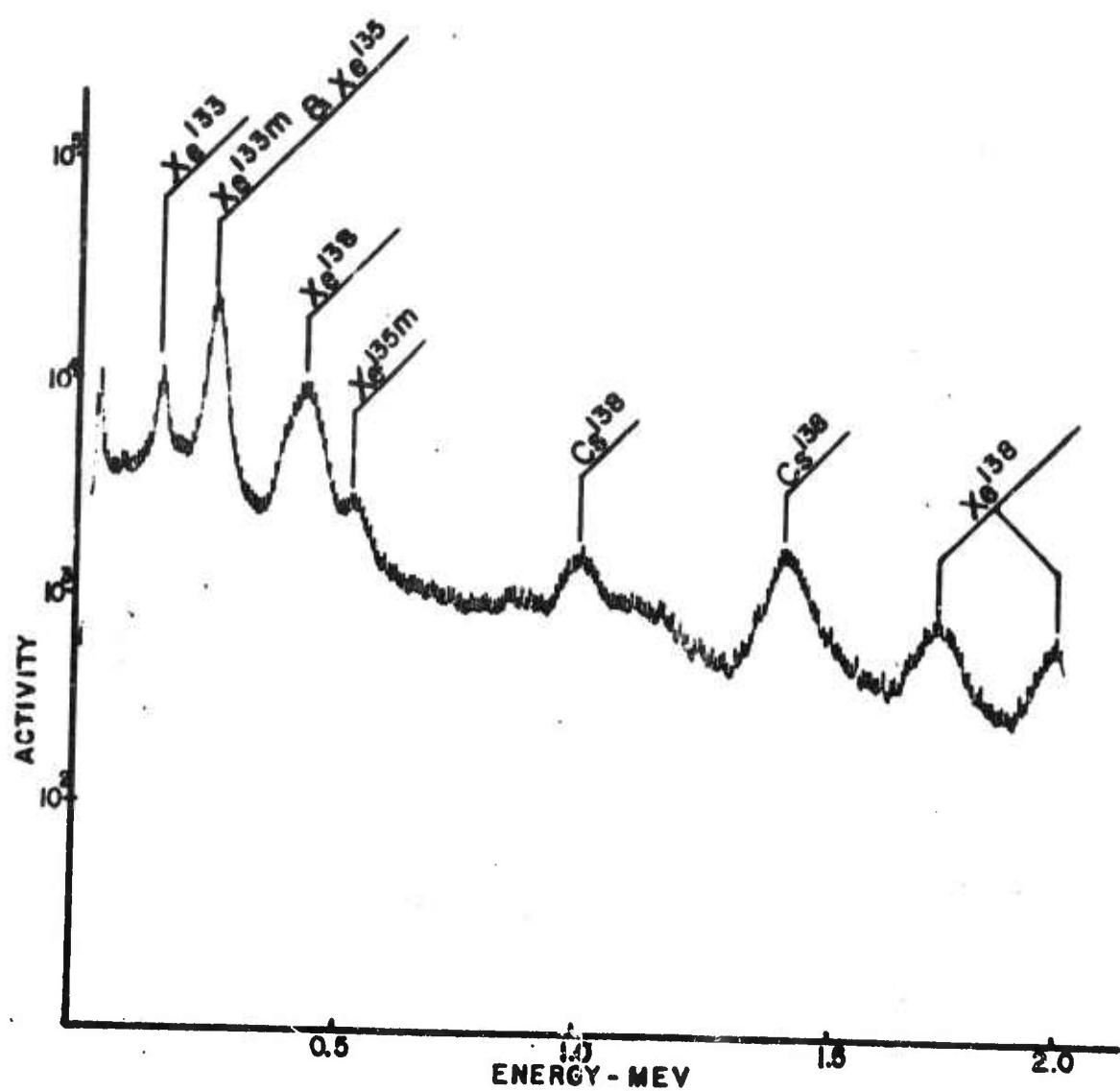
Figure 4. Gamma ray spectrum of krypton trapped after chromatographic separation. Measurement made approximately 36 minutes after irradiation and 2 minutes after separation.
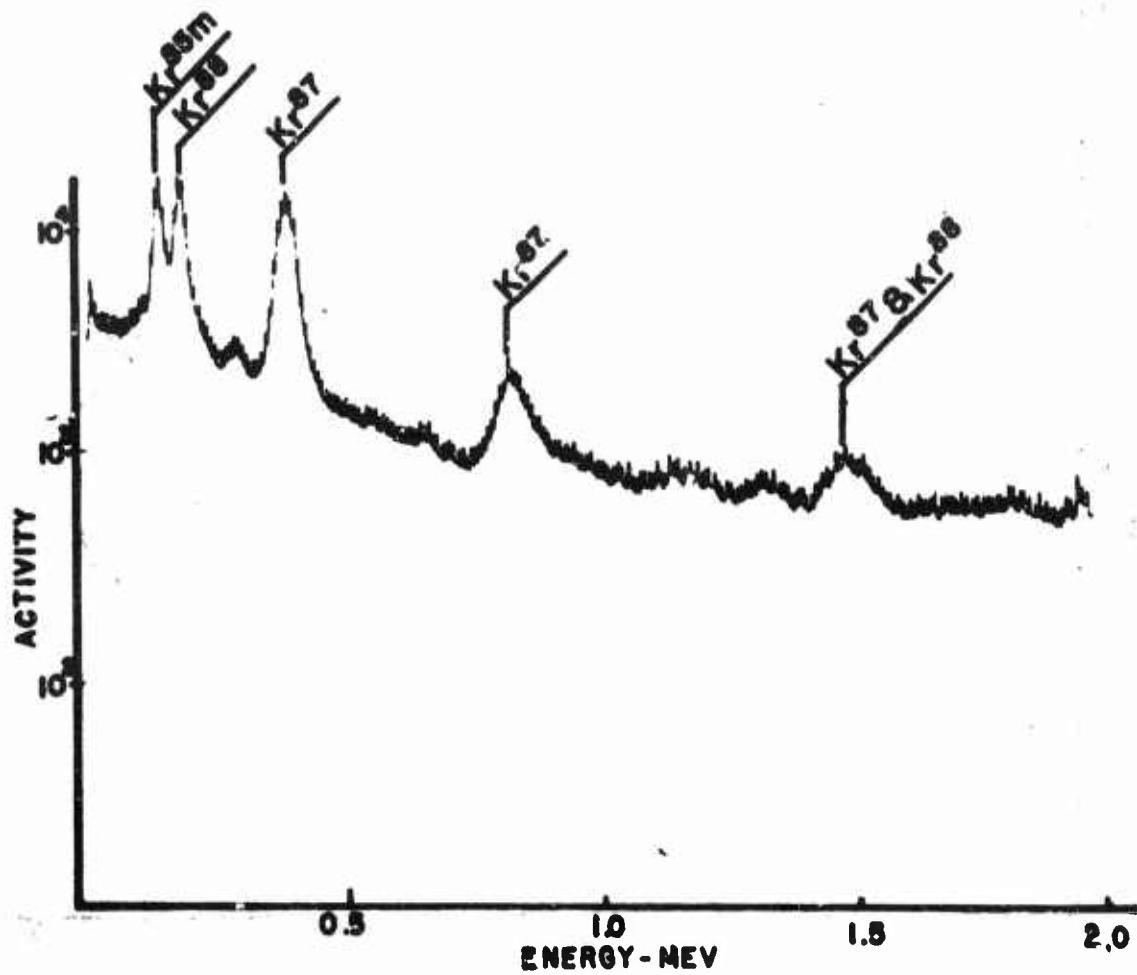
Figure 5. Gamma ray spectrum of xenon trapped after chromatographic separation. Measurement made approximately 51 minutes after irradiation and 15 minutes after separation.

The eluted gases contained most of the activity of the original sample. Some activity still remained on the charcoal column, however. Gamma spectra of the remaining active species are shown in Figure 6. Initially only the decay products of xenon and krypton were identifiable. Later, two iodine isotopes were evident and still later, Figure 7, another iodine isotope is identifiable.

A list of all the radioactive species identified is presented in Table II. Half lives used in the identification were determined using the computer program Frantic II, developed at M.I.T.(7).

4. Discussion

    a. Proposed mechanism of polyethylene degradation

    The agreement with Laskaris on the amount of hydrogen present in the degradation products is good and quite different than that generally reported (1). This indicated that the mechanism proposed in the literature is incorrect or the conditions in this study are sufficiently different to cause a different reaction. The latter would appear to be the case as the conditions in this experiment are different than any found in the literature.

    While no studies were undertaken to specifically identify the mechanism of the polyethylene degradation in the AG-201 reactor fuel, the following seems logical in view of the products formed. The AGN-201 fuel as mentioned earlier, contains the UO_2 evenly distributed throughout the polyethylene. When undergoinf fission, the massive fission products subject the polyethylene to more severe ionizing effects than other irradiation techniques. Scissions

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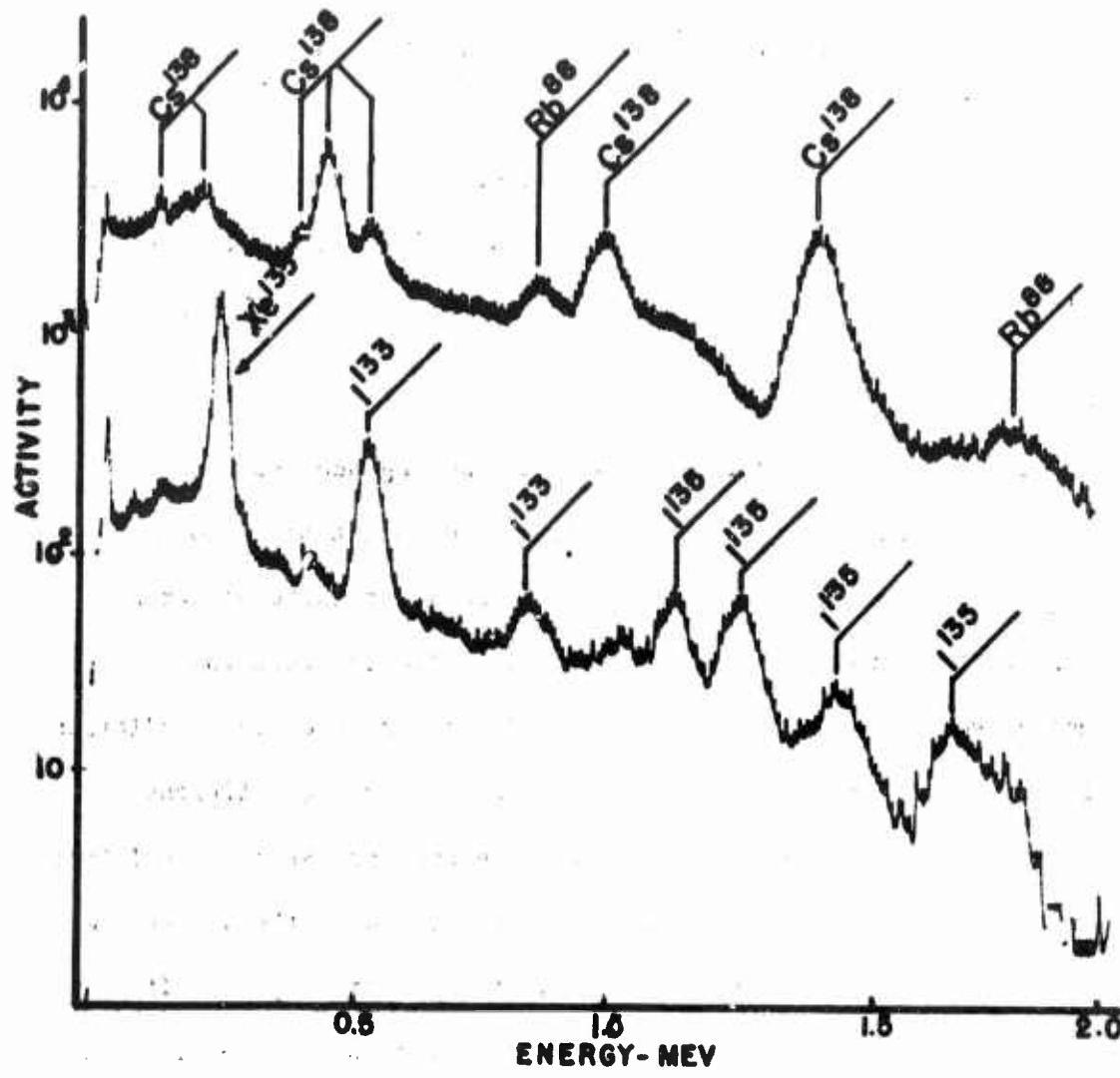
Figure 6. Gamma ray spectra of species not eluted from charcoal during gas chromatographic separation. Spectrum 1 measured at 44 minutes after irradiation; spectrum 2 at 425 minutes after irradiation.
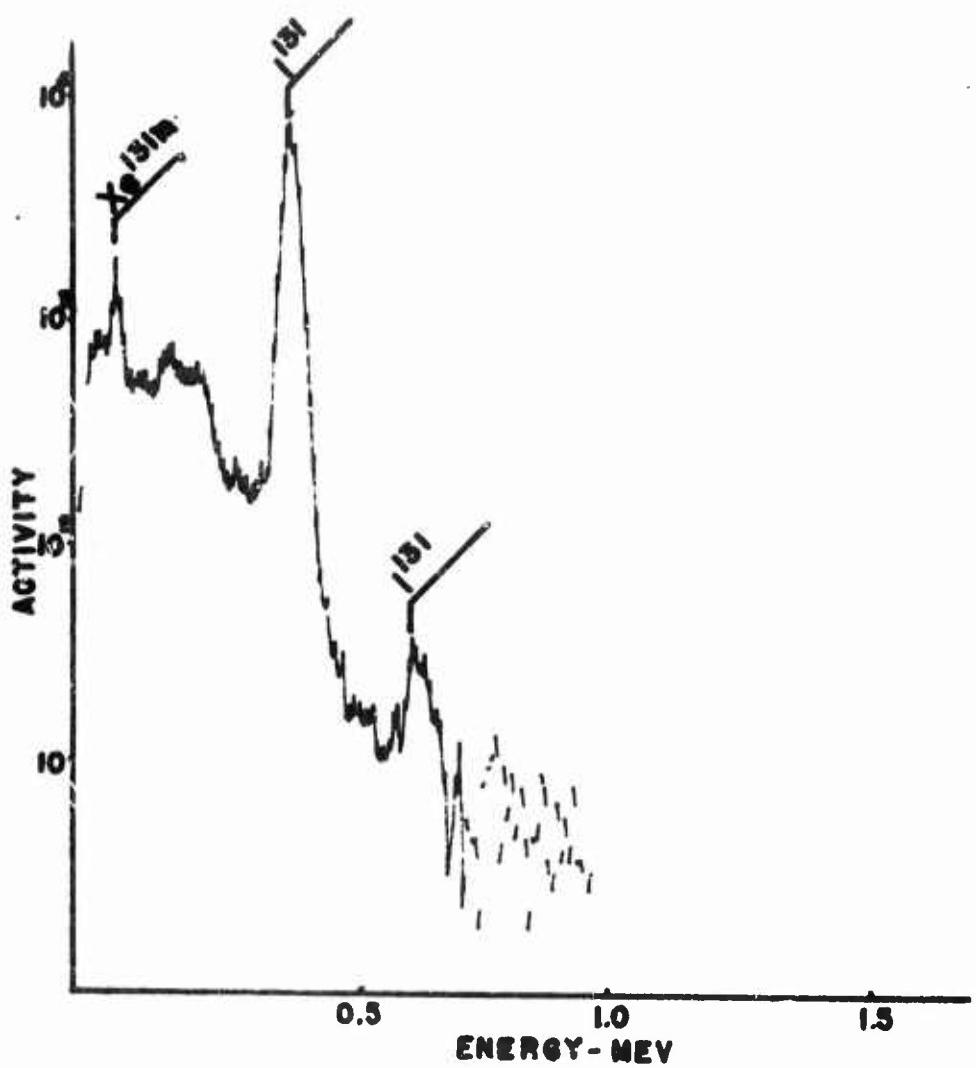
Figure 7. Gamma ray spectrum at species not eluted from charcoal during gas chromatographic separation. Measurement at 6 1/4 days after irradiation.

TABLE II

RADIOACTIVE SPECIES IDENTIFIED IN THE

REACTOR FUEL DECOMPOSITION PRODUCTS

A. Well identified isotopes

Isotope	Half-life
Kr^{85m}	4.4 hours
Kr^{87}	1.3 hours
Kr^{88}	2.8 hours
Xe^{133m}	2.3 days
Xe^{133}	5.3 days
Xe^{135}	9.2 hours
Xe^{138}	17.0 minutes
I^{131}	8.0 days
Cs^{138}	32.2 minutes

B. Less well identified isotopes (generally photopeak identification only--no supporting half life data)

Rb^{88} Rb^{89} Xe^{131m} Xe^{135m} I^{133} I^{135}

along chains, breakage at side-chain junctions, and fur:her
ionization of the newly formed fragments should all occur.
Likely steps leading to the various hydrocarbons are:

1. Formation of radicals

$$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}- \longrightarrow -\overset{|}{\underset{|}{C}}-\overset{\bullet}{\underset{|}{C}}- + H^\bullet$$

$$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}- \longrightarrow -\overset{|}{\underset{|}{C}}\bullet + \bullet\overset{|}{\underset{|}{C}}-$$

$$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\bullet \longrightarrow -\overset{|}{\underset{|}{C}}\bullet + \bullet\overset{|}{\underset{|}{C}}\bullet$$

$$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\bullet \longrightarrow \overset{|}{\underset{|}{C}}\bullet + \bullet\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\bullet$$

2. Radical combination

$$H^\bullet + H^\bullet \longrightarrow H_2$$

$$-\overset{|}{\underset{|}{C}}\bullet + H^\bullet \longrightarrow CH_4$$

$$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\bullet + \colon \longrightarrow C_2H_6$$

$$\bullet\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\bullet + \bullet\overset{|}{\underset{|}{C}}\bullet \longrightarrow \overset{\times}{\underset{\searrow}{C}}-\overset{}{\underset{}{C}}$$

3. Abstraction of H

$$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}- + CH_3^\bullet \longrightarrow CH_4 + -\overset{|}{\underset{|}{C}}-\overset{\bullet}{\underset{|}{C}}-$$

$$\overset{|}{\underset{|}{C}}\bullet\overset{|}{\underset{|}{C}}- + H^\bullet \longrightarrow -\overset{|}{\underset{|}{C}}-\overset{\bullet}{\underset{|}{C}}- + H_2$$
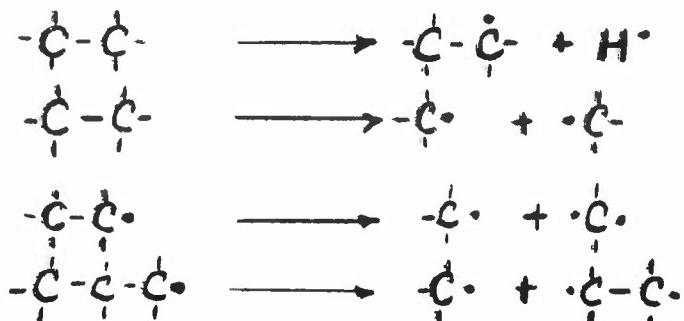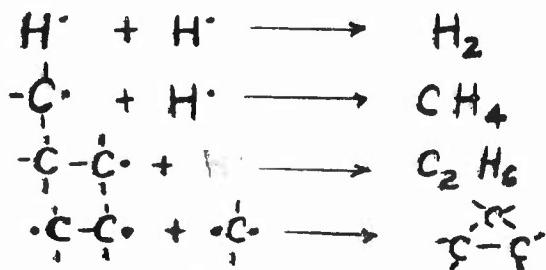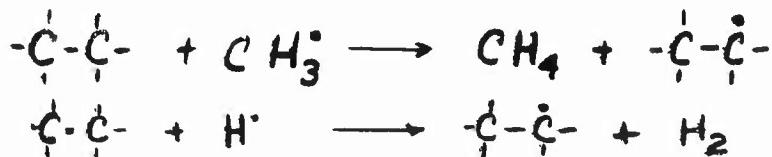
4. Radical Disproporation

$$-\overset{|}{\underset{|}{C}}-\overset{\bullet}{\underset{|}{C}}\bullet \longrightarrow \overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}}$$

$$\bullet\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\bullet \longrightarrow \bullet\overset{\nearrow C \nwarrow}{\underset{}{C}}-\overset{}{\underset{}{C}}\bullet$$
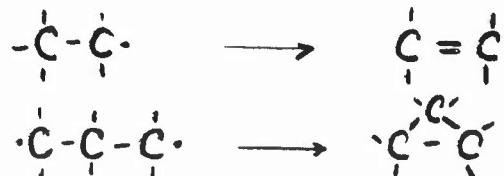
The proposed steps in the reaction are very similar to those by several investigators, e.g., Miller et.al. (8), the principal difference being the larger amount of fragmentation. As stated earlier the more severe ionizing effect of the massive fission fragments can be expected to produce more fragments than perhaps gamma radiation used for most studies. There is some evidence that the proportional yield of hydrogen is dependent on the total radiation dose, decreasing at the higher doses. This would support the supposition that the difference of hydro-carbon content is due to the greater ionization effect of the fission fragments.

b. Separation of xenon and krypton in tra quantities

The separation of krypton and xenon by a gas-solid chromatographic technique is not new. The excellent separation of trace quantities of the two gases in such short time is significant. The gamma spectra of the trapped gases are very accurate aids in identification.

It should be pointed out however that an attempt to detect xenon as it eluted at about 95°C was not successful even though it was trapped in the same manner as described above. Apparently at that temperature the elution of the xenon is to slow to be practically detected. The higher temperature appears to be necessary to elute the xenon in the trace quantity used in this study.

c. Identification of halogens that may be present

Iodine and bromine were both suspected as being present in the gaseous products. It had been hoped that separation of

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the xenon and krypton from the remaining volatile products would allow their identification. As expected, the more active decay products of short half life xenon and krypton isotopes dominated the gamma ray spectra initially. Iodine was identified after most of the xenon and krypton daughters had decayed sufficiently. No bromine could be identified even then. Bromine 83 is the only bromine isotope that could likely have been present at the time the later gamma spectra were measured, as the other shorter life isotopes would have decayed completely by that time. A more rapid sampling and separating technique may enable one to more accurately identify species other than krypton and xenon.

Since iodine is detectable in the volatile products, the question immediately arises as to its form. While it is entirely possible that it could be molecular iodine, this seems quite unlikely in view of the large amount of atomic hydrogen and organic radicals likely present during irradiation. It logically appears that any iodine present would be in the form of hydrogen iodide or low hydrocarbon compounds such as methyl iodide.

5. Conclusions

a. The irradiation of polyethylene by an internal source, i.e., the UO_2 in the AGN-201 fuel, results in a lower ratio of hydrogen to hydrocarbon than irradiation using an external radiation source. This is apparently caused by the large number of highly ionizing fission particles which increase the actual ionizing dose to which the polyethylene is subjected during irradiation.

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b. The amount of xenon and krypton produced in the relatively small sample of AGN-201 fuel by short irradiation can be separated by solid-gas chromatography and detected by scintillation counting techniques without isotopic dilution.

c. Iodine is present in the volatile products from the AGN-201 fuel.

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APPENDIX I

List of Equipment Used

Gas Chromatograph: Fisher-Hamiltion Model 29 Gas Partitioner
with a 6 ft. x 1/4 in. 30% Hexamethyl-phosphoramide (HMPA)
on 60/80 mesh columnpack in position 1 and a 12 ft. x 1/4
in. composite two part column consisting of 5 ft. of
uncoated 60/80 mesh columnpack followed by 7 ft. of 42/30
mesh activated molecular sieve 13X in position 2.

Recorder for Gas Chromatograph: Varian Model 14, 1 milivolt
recorder.

Scintillation Crystal and Associated Equipment:
2 in. x 2 in. NaI(TI) crystal
DuMont Type 6292 Photomultiplier Tube
Hewlett-Packard Preamplifier Model
Technical Associates Rate Meter Model FM 1

Vacuum System: A glass vacuum system with a CENCO HYVAV 2 pump
and an oil diffusion pump. Pressure measurement: Thermo-
couple gauge caliberated to 1 micron. (Pressures actually
used were lower than this and were estimated to be 10^{-4} mm
when the meter was "pegged").

Reaction Vessel: A cylinderical aluminum container approximately
2 x 5 in. fitted with a vacuum stainless steel valve. (It
proved necessary to attach a high vacuum stopcock to the
valve in order to maintain the desired vacuum when the
vessel was disconnected from the vacuum system for irrad-
iation.)

Fuel: 8 grams of UO_2 in approximately 200 grams of polyethylene.

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13. ABSTRACT

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14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Gas Chromatography						
Spectral Analysis						
Hydrogen						
Hydrocarbons						
Reactor						
Fuel						
Gas						
Core						
Xenon						
Krypton						

DD FORM 1473 (BACK)

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